

GEORGIA INSTITUTE OF TECHNOLOGY  
Engineering Experiment Station

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with the Products of Wood Burning  
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Sponsor: Georgia Forest Research Council  
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# GEORGIA INSTITUTE OF TECHNOLOGY

## Engineering Experiment Station

### PROJECT TERMINATION

Date 8/30/71

PROJECT TITLE: Identification of the Pollution Hazards  
Associated with the Products of Wood Burning.

PROJECT NO: B-387

PROJECT DIRECTOR: Dr. John Burson

SPONSOR: Georgia Forest Research Council

TERMINATION EFFECTIVE: 3/31/71

CHARGES SHOULD CLEAR ACCOUNTING BY: 8/1/71

Final report submitted 8/27/71.

Chemical Sciences & Materials Division

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FINAL REPORT

PROJECT B-387

IDENTIFICATION OF POLLUTION HAZARDS ASSOCIATED WITH THE PRODUCTS OF WOOD  
BURNING

JOHN H. BURSON, III AND EDWARD Y. H. KENG



Covering the Period

October 1, 1970, through May 31, 1971



Engineering Experiment Station  
GEORGIA INSTITUTE OF TECHNOLOGY  
Atlanta, Georgia

Prepared for

GEORGIA FOREST RESEARCH COUNCIL  
POST OFFICE BOX 823  
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GEORGIA INSTITUTE OF TECHNOLOGY  
Engineering Experiment Station  
Atlanta, Georgia

FINAL REPORT

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## TABLE OF CONTENTS

I. SUMMARY	-----	1
II. INTRODUCTION AND SPECIFIC AIMS	-----	2
III. EFFECTS OF SPECIFIC POLLUTANTS	-----	4
IV. PERTINENT LITERATURE REFERENCES	-----	8
V. CONCLUSIONS AND RECOMMENDATIONS	-----	27

## I. SUMMARY

The contribution from the products of wood combustion to the national air pollution level is very small. However, significant aesthetic objections have been voiced regarding the deterioration of local environments from wood burning products. To date, these objections have been concerned primarily with decreased visibility and undesirable fall-out from the heavy particulate burden that is characteristic of woody combustion. The role of photochemical smog formation from woody fuels combustion products is unresolved at present. However, the most pessimistic estimates of the degree of photochemical smog formation from woody combustion products is still hundreds of times less than that resulting from fossil fuels combustion.

Pertinent references have been obtained from the open literature and assembled in the form of an annotated bibliography. Hopefully, this study will serve as a logical basis for developing meaningful research programs in this area. The major areas in need of further research have been identified and priorities assigned for their completion.

## II. INTRODUCTION AND SPECIFIC AIMS

Combustion processes constitute one of the major sources of air pollution in the United States. One important source of particulate pollutants is agricultural burning. For example, a typical grass fire extending over one acre is estimated to produce  $10^{22}$  particulates. Particulates from such sources certainly have an undesirable æsthetic effect; however, their long range implications as truly harmful pollutants are much more uncertain. Agricultural fires, of course, may be either intentional or accidental. If the former, they are usually referred to as prescribed burns and are used primarily for control of agricultural diseases, insect infestations, and disposal of wastes. In the South alone, more than a million acres of forest and range land are subjected to fire treatments of one form or another each year.

Fire has been used as an effective tool in forestry practice and in agriculture for many years; however, it is generally recognized that the use of fire for these purposes can and does contribute to local air pollution. The more serious long range air pollution aspects of such agricultural burnings have of late begun to receive increasing attention.

The purpose of this study was to determine if definitive information is available regarding possible harmful effects from pollutants that originate from wood burning operations with special emphasis given to possible photochemical effects. Wood burning operations as used in this context include conventional agricultural burning and operations primarily of an incineration nature such as the disposal of sawdust and wood chips. The primary source of information collected has been from the open literature; however, other sources of information such as internal reports of the

Environmental Protection Agency, reports and pamphlets published by other agencies, and personal contacts with researchers knowledgeable in the field have also been utilized. The ultimate reason for this effort was to acquire solid scientific evidence that either confirms or refutes allegations that wood burnings may constitute a serious air pollution hazard. With such a factual and objective background, meaningful recommendations can be made as to the extent and nature of anti-pollution legislation that may be proposed and, perhaps more importantly, those areas needing further study can be identified and priorities assigned for their completion.

This report is thus intended as a basis from which further research efforts can emanate. The continued vigor and prosperity of the forest related industries of this State demands that aggressive, informed leadership be available not only to meet but to anticipate the demands of modern day society.

### III. EFFECTS OF SPECIFIC POLLUTANTS

#### A. Photochemical Effects

Most of the research effort to date regarding photochemical aspects of wood burning has been conducted on the West Coast, primarily in California and Oregon. Early field studies indicated that the concentrations of photochemically active hydrocarbons were generally negligible at a mile or more from the combustion source. However, later studies using more sophisticated instrumentation indicated that emissions from land clearing operations may contribute a significant burden to the level of photochemically active hydrocarbons. Insofar as could be determined, the extent to which these candidate hydrocarbons actually participate in photochemical reactions has not been confirmed by quantitative studies for any wood burning operations.

#### B. Oxides of Nitrogen

Oxides of nitrogen are generally associated with either high temperatures of combustion in the presence of air or the decomposition of nitrogen containing molecules such as proteins. Neither of these conditions exists to an appreciable extent in wood burning, thus oxides of nitrogen pose no particular problem in wood burning. For example, NO<sub>x</sub> concentrations in the immediate vicinity of open brush fires ranged from 21 to 42 ppm; whereas NO<sub>x</sub> concentrations in automobile exhausts are reported to be greater than 1000 ppm.

#### C. Oxides of Sulfur

No significant concentrations of sulfur oxides have been reported to result from combustion of woody fuels.

#### D. Oxides of Carbon

Carbon monoxide levels within 60 feet of an open slash fire were found to be 40 ppm, decreasing to 10 ppm at 150 feet from the fire. These values are less than the maximum allowable human exposure levels for an 8-hour period.

Carbon dioxide concentrations were found to be 1000 ppm at 60 feet from the fire edge, dropping to 500 ppm at 150 feet. Aircraft measurements of plume traverses reported increases of about 250 ppm in CO<sub>2</sub> concentrations up to 25 km. from the fire. Maximum allowable concentrations permit exposures of up to 5000 ppm.

#### E. Hydrocarbons

Hydrocarbons released by the incomplete combustion of fuels, fossil or wood, are important to maintenance of air quality standards. Photochemical reactions frequently result from the interaction of light gaseous hydrocarbons with ozone in the presence of oxides of nitrogen and intense sunlight. The resultant photochemical smog is usually much more objectionable than the original emissions. The eye irritation and respiratory difficulties experienced by Southern California residents results largely from such photochemical reaction products.

The open burning of woody fuels, particularly green materials, often produces large amounts of hydrocarbons. However, all available evidence indicates that the quantity capable of undergoing photochemical reactivity of the type described previously is small.

Open burning of dry wood has been shown to yield up to 4.7 lbs. of hydrocarbon per ton of fuel and green brush up to 27.4 lbs. per ton. By comparison, the automobile produces ten times as much hydrocarbon per lb. of

fuel than open burned, woody fuel; 15 times as much carbon monoxide; and up to 20 times as much nitrogen oxides. Thus it appears that the types and amounts of hydrocarbons generated by combustion of woody fuels may be relatively unimportant to the formation of photochemical smog. However, laboratory studies must be made as has been done for automobile exhaust components before definite conclusions can be drawn

Naturally occurring hydrocarbon emissions from vegetation, i.e., in the absence of combustion, include isoprene and alpha-pinene, both of which have been shown to undergo photochemical reaction. Studies are needed to determine the character of the resulting photochemical reaction products and the extent of their contribution to the "background level" of air pollution.

#### F. Particulate Matter

Combustion of woody fuels produces large quantities of particulates, ranging from about 9 lbs. per ton of dry wood in open burning to 25 lbs. per ton when burned in a single-chamber incinerator. In terms of particulate numbers, the previous mass values assume values on the order of  $10^{22}$  particles per acre of open grass fire.

Prescribed agricultural burnings are estimated to produce less than two per cent of the national particulate burden from urban-industrial and rural-agricultural sources. Forest fires, however, are a more prolific source, producing up to five times more particulate matter than do prescribed burns.

Particulates probably constitute the most serious class of pollutants from combustion of woody materials. The most obvious objection to these pollutants is the impairment of visibility and the esthetic objections to fall-out of carbonaceous materials. A secondary and perhaps more serious

objection is the weather modifications that may result from such a burden of hygroscopic particulates which then may act as condensation nuclei. The usual objections to atmospheric particulates in the presence of  $\text{SO}_2$ , such as the deleterious effect on materials of construction and as reaction sites for photochemical processes, are difficult to judge for woody emissions since  $\text{SO}_2$  is not a significant factor in most cases.



#### IV. PERTINENT LITERATURE REFERENCES

##### A. Wood Burning and Effects on the Environment

1. Boubel, R. W., M. Northcraft, A. Van Vliet, and M. Popovich, "Wood Waste Disposal and Utilization," Engineering Expt. Station, Oregon State College, Oregon, Bulletin #39 (1958).

The objective of the research and of this publication was the development of information which could be applied in a practical manner to materially reduce nuisance created by fall out of cinders and other unburned materials from wood burning operations. Part I covers a study of sawmill waste burners. Part II is a critical study of the wood waste market and cost of delivery to markets, with a view of encouraging utilization of materials now burned. (Authors' Summary condensed. Includes an exhaustive list of references).

2. Boubel, R. W., E. F. Darley, and E. A. Schuck, "Emissions from Burning Grass Stubble and Straw," J. Air Poll. Control Assoc. 19, (7), 497-500 (1969).

The emissions from burning the residue following grass-seed harvest were determined by means of a combined laboratory-field study. Samples of the straw and stubble residue were burned in the laboratory burning tower at the University of California at Riverside. Complete analyses were determined for gaseous and particulate emissions for the important grass species from the Willamette Valley of Oregon. Particulate emissions averaged 15.6 lb/ton of fuel burned. Carbon monoxide averaged 101 lb/ton of fuel burned. Hydrocarbon emission averages, in pounds per ton of fuel burned, were 1.74 for saturates plus acetylene, 2.80 for olefines, and 1.68 for ethylene. The NOx emission, at the temperature peak during the burn, averaged 29.3 ppm. Field studies, conducted by personnel from Oregon State University, measured only particulate emissions, carbon dioxide, and temperature over the burn. The carbon dioxide values were found to be similar to those obtained on the burning table at UCR and it was therefore concluded that the other gaseous emissions were similar and could be used as reasonably accurate for emission inventories. The temperature values obtained in the laboratory and field were also similar and further justifies extrapolating the burning table data to field situations. The particulate matter collected in the field studies averaged 15.55 lb of particulate per ton of fuel burned. This is the same average obtained for the burning table data which again serves to validate the emissions reported from Riverside. Much more variability was found in the particulate emissions obtained in the field which reflects the wider range of environmental conditions encountered in the field.

3. Brady, N. C., "Agriculture and the Quality of our Environment," Amer. Assoc. for the Advancement of Science, Washington, D. C., 460 pp. (1967).

A detailed discussion of the varied aspects of agricultural operations on ecological, economical and demographic factors.

4. Brandt, C. S., "Agricultural Burning," J. Air Poll. Control Assoc., 16, (2), 85-6 (1966).

Open burning is used in agricultural practice for agricultural waste disposal, disease control, and land and crop management. The relationship between the necessary use of fire and the problems of air pollution control is discussed. (15 references)

5. Brender, E. V., and Cooper, R. W., "Prescribed Burning in Georgia's Piedmont Loblolly Pine Stands," J. Forestry, 66, 31-6 (1966).

A discussion and description of open burning techniques currently practiced and some economic and ecological factors to be considered.

6. Browne, F. L., "Theories of Combustion of Wood and Its Control," Forest Products Research Laboratory Publication, Rept. #2136, U.S. Dept. of Health Agriculture and Eng. (1958).

Substantial progress has been made in reaching an understanding of the fundamental mechanisms of the pyrolysis and combustion of wood and alteration from added chemicals. No single theory completely describes the manner in which resistance to fire is imparted to wood. An exhaustive survey of literature is made by the author. (Author's conclusions, 10 tables, and 140 references).

7. Byram, G. M. (edited by K. P. Davis), "Combustion of Forest Fuels," Forest Fire Control and Use, McGraw Hill Book Co., Inc., 61 and following, (1959).

Discussed in this article are the combustion process, chemistry of combustion, phases of combustion, combustion and the energy yield, heat losses, factors affecting the rate of energy release, and related areas in combustion of forest fuels.

8. Davis, J. B., "Forest Fire Control Decision Making Under Conditions of Uncertainty," J. Forestry 66, 626-31 (1968).

Game theory and decision theory could help a fireboss evaluate strategies to use in forest fire control. This paper describes several types of matrix games, subjective utility, and various criteria for strategy selection. It shows, in scenario forms, how decision theory might be used in a fire-fighting problem.

9. Dell, J. A. and L. R. Greene, "Slash Treatment in the Douglas-Fir Region," J. of Forestry 66, 610-4 (1968).

Logging slash is a critical problem in the Douglas-fir region of the Pacific Northwest. It constitutes a serious fire hazard and is costly to eliminate. And its treatment by burning is a growing source of concern to air pollution control specialists. Present trends in slash treatment include streamlining the use of prescribed burning, developing other physical, mechanical, and chemical means of disposing, and--most desirable of all methods--utilization of logging waste. Among the fire control techniques

that have been adapted or tested for slash treatment are chemical fire retardants, sprinkler systems, firing with drip torches or fuses, electric ignition circuitry, remote ignition, and portable incinerators. Nonburning treatment of slash includes lopping and scattering, lopping and leaving in place, chipping by mechanical chippers, disking or trampling with crawler-type tractors, burying, and leaving slash on the ground to decompose.

10. Feldman, E. S. and L. M. Rosnick, "Wood Waste Disposal and Air Pollution Control in the Los Angeles Area," Forest Products Research Society, #56 (1949).

The intensification of the air pollution problem in the Los Angeles basin combined with a comprehensive set of regulations regarding air pollution adopted by the last California legislative have focused attention on waste disposal methods used by wood-working plants in the area. Cheap oil fuels make the use of wood waste for fuel purposes uneconomical and incineration is the common disposal method. Incomplete combustion during incineration is the primary cause of pollution. Analysis is made of the quantity of wood waste, methods of disposal, principles of combustion and incinerator design, better operation of existing equipment, and conversion and reduction of waste. (14 references).

11. Foster, W. W., "The Size of Wood Smoke Particles," Intern. J. Air Poll. (London) 3, 89-96 (1960).

The smoke generated when wood is heated in air contains a considerable range of compounds resulting from the distillation and degradation of cellulose, lignins, resins, and tannins. Visible particles which are formed when the smoke cools appear to equilibrate rapidly with the ambient vapors. In the present experiments smoke was generated by agitating sawdust fed into a blast of air which was at a temperature of  $314 \pm 2^{\circ}\text{C}$ . Smoke which cooled to room temperature was sampled in 3 ways: 1. by means of a cascade impactor, 2. by gravitational settling in a chamber about 10 cm. high, and 3. by an electrical method. Measurements of the rate of coagulation of charged aerosols is difficult, chiefly because the particles deposit rapidly on the containing walls. Although the results presented cannot be considered to be conclusive, it would seem that the method of determining the average radius of charged aerosols might be useful when studying their coagulation, especially when applied to aerosols initially monodisperse of of known size distribution. (11 references).

12. Fritschen, L., H. Bovee, K. Buettner, R. Charlson, L. Monteith, S. Pickford, J. Murphy, and E. Darley, "Slash Fire Atmospheric Pollution," Pacific Northwest Forest and Range Exp. Sta., U.S.D.A. Forest Serv. Res. Pap. PNW-97, 42 pp. (1970).

A discussion of atmospheric pollution levels resulting from instrumented and controlled open burning.

13. Gerstle, R. W. and D. A. Kemnitz, "Atmospheric Emissions From Open Burning," J. Air Poll. Control Assoc., 17, (5), 324-7 (1967).

Emission data have been derived from the simulated open burning of municipal refuse, landscape refuse, and automobile components. The data confirm that disposal of refuse by open, uncontrolled burning invariably leads to higher emissions than incineration and creates an unnecessary air pollution problem.

14. Grohse, E. S. and L. E. Saline, "Atmospheric Pollution: The Role Played by Combustion Processes," J. Air Poll. Control Assoc. 8, (3), 255-67 (1958).

The article describes nature and causes of air pollution from combustion processes. It provides information on smoke, fly ash and  $\text{SO}_2$  from such processes. Effects of  $\text{SO}_2$  as an air pollutant and its removal are discussed. (Authors' conclusions and 21 references).

15. Gunlogson, G. B., "Environmental Problems - A New Area of Engineering for the 70's," Agricultural Engineering 51, 277-8 (1970).

A discussion of the challenges that environmental problems pose for the new and old agricultural engineer.

16. Hodgson, Athol, "Control Burning in Eucalypt Forests in Victoria, Australia," J. Forestry 66, 601-3 (1968).

Fire has been a factor in the eucalypt forest environment for thousands of years. In this period the flora and fauna developed the ability to live in balance with widespread and repeated fires. In recent times, colonization and the demands of a modern society have reduced the forest area, altered the composition of the forests and created new values in the forests. Fires with intensities above 500 BTU/sec/ft cause severe damage to these values; those of low intensity do little or no measurable damage. The intensity of wildfires and the difficulty of controlling them is a function of severe weather and the amount of fuel available for burning. Doubling the available fuel usually doubles the rate of spread of the fire and increases its intensity fourfold. Control is made extremely difficult by mass short-distance spotting from stringybark fuel and spectacular long-distance spotting from candlebark fuels. Control burning over large areas to keep fuel quantities below six tons per acre cheaply and effectively reduces the incidence of high intensity wildfires and minimizes damage. Guidelines have been prepared to assist foresters plan and manage these fires.

17. Johnson, A. J. and G. H. Auth, "Fuels and Combustion Handbook," McGraw-Hill Book Co. Inc., New York, 106-128 (1951).

A summary of data on burning of wood bark and refuse; agricultural products and agricultural wastes with detailed discussion and pertinent references is given. Information on general characteristics of wood, ultimate analyses and heating value of typical woods and industrial uses of wood waste is also provided.



18. Johnson, H. C., and H. A. James, "Controlled Open Burning in the San Francisco Bay Area," J. Air Poll. Control Assoc. 20, 530-3 (1970).

The conditions most conducive and most damaging with regard to open burning are discussed.

19. Kaiser, E. R., "The Incineration of Bulky Refuse - II," Proceedings of 1968 National Incinerator Conference, New York, N.Y., 129-33 (1968).

Incineration of green logs, brush demolition lumber and the like in a hearth type of furnace is discussed. Burning rates averaged 18 lb/hr/sq ft of refractory hearth area. Secondary combustion space is necessary to burn smoke that is generated in the furnace. Fly ash emission is low because of minimal flow of underfire air. Proposed designs for incineration of 2 to 20 tons/hr. are shown.

20. Kaiser, E. R., "Prospects for Reducing Particulate Emissions from Large Incinerators," J.A.P.C.A. 20, 324 (1970).

Conventional types of municipal incinerators generate enormous quantities of stack gas because of high excess air and high temperatures. Under these conditions the size and cost of equipment to clean the flue gas to low dust contents are large. By burning the refuse in boiler furnaces at low excess air, and generating steam, the volume of flue gas to be cleaned is reduced to a minimum. Where high efficiency of flue-dust collection is required, steam generation from refuse firing permits a major saving on the cost of dust collection.

21. Kohn, R. E., "Leaf Burning: An Economic Case of Study," Scientist and Citizen 9, 71-5 (1967).

A benefit/cost analysis is applied to leaf burning to determine whether the benefits of control outweigh the costs to community. Estimation of pollution risks, appraisal of associated risks, costs of control and process substitution effect on control costs are discussed. (19 references).

22. Kreichelt, T. E. (Robt. A. Taft San. Eng. Ctr. Cincinnati, Ohio), "Air Pollution Aspects of Teepee Burners," U.S. Dept. of Health, Education, and Welfare, Public Health Service; Publication #999-AP-28, 35 pp. (1966).

This report covers an evaluation study of air pollution emissions based upon extensive literature search and field trips to 15 teepee burners in 6 states. Smoke as a function of composition and rate of charge was observed and the effect of burn charging methods, construction and operational procedures on smoke emissions, recorded. None of the teepee incinerators observed in operation met normal visible emission limitations of air pollution control ordinances of most municipalities. Nuisance problems from fly ash fall out can be expected within distances up to 1290 ft. downward from an operating teepee. (Includes 9 tables, 17 figures, appendix, and 7 references).

23. Madonna, L. A., "The Pollution System - A Chemical Space Model," Brit. Chem. Engr., 15, 1149-53 (1970).

The author shows how the consumption of certain effluent chemicals in the atmosphere can be put into chemical space form, and how linear network theory can be applied once the chemical model relationships have been expressed in network matrix equation form. A new method of representing a chemical system allows the pollution model to be constructed, and simplifies the analysis of the time-varying chemical models typical of the pollution system.

24. Magill, P. L. and R. W. Benoliel, "Air Pollution in Los Angeles County: Contribution of Industrial Products," Ind. Eng. Chem., 44, 1347 (1952).

Emission data on chemicals to Los Angeles atmosphere from wood waste incinerator effluent are summarized.

25. Meland, B. R. and R. W. Boubel, "A Study of Field Burning Under Varying Environmental Conditions," J. Air Poll. Control Assoc. 16, (9), 481-4 (1966).

Grass field burning in the Willamette Valley of Oregon contributes a high concentration of pollutants to the atmosphere during August and September each year. Approximately 233,000 areas of grass seed land are burned after the harvest. Reasons for burning following a harvest are: 1. to control plant diseases, weeds and insects 2. to eliminate surface organic matter, and 3. to promote return of nutrients to the soil. Serious air pollution problems result from this burning. The study was made to determine whether conditions exist when significant air pollution reduction can be achieved. The dependent variables measured were particulate emission and size distribution, combustion temperature, burn rate, amount of ash, per cent of organics in the particulate, and smoke appearance. (5 references).

26. Murphy, J. L., L. J. Fritschen, and O. P. Cramer, "Research Looks at Air Quality and Forest Burning," J. of Forestry, 530-5 (1970).

The present state of knowledge and current research efforts on forest burning and air quality are discussed. Possible air pollution control measures are presented. Included are meteorological smoke management and fire behavior management. Slash disposal methods other than burning are reviewed.

27. Netzley, A. B. and J. E. Williamson, "Multiple Chamber Incinerators for Burning Wood Waste," Air Pollution Engineering Manual, U.S. Dept. of Health, Education and Welfare; Public Health Service; Edited by J.A. Danielson, 436-47 (1967).

Burning of wood waste may be accomplished by open burning, burning in single chamber incinerators (including the tepee and silo structures), and burning in multiple chamber incinerators. Of these, the latter is the most satisfactory from an air pollution standpoint. Burning of wood waste in open areas and at dump sites or in single-chamber incinerators is accompanied by dense clouds of smoke, fly ash, and disagreeable odors. These air contaminants are, basically, due to incomplete combustion and are discharged in the form of particulate matter, aldehydes, hydrocarbons and organic acids, as

well as smoke and fly ash. Smoke and particulate emissions from multiple-chamber incinerators are reduced significantly, since more complete combustion is promoted in the multiple chambers. Detailed discussion of the design procedure and an illustrative design for multiple-chamber incinerators are included.

28. Neuberger, H., "Condensation Nuclei: Their Significance in Atmospheric Pollution," Mech. Eng., 70, (3), 221-5 (1948).

The author provides information on the atmospheric constituents, condensation nuclei and their chemical nature, the sources of such nuclei (which include combustion products from forest and tepee fires), physical properties of nuclei and biological effects of aerosol. (Author's bibliography, includes 20 references).

29. Porter, Earl, "A History of Forest Fire Prevention on International Paper Company Southern Timberlands in the Past 35 Years," J. Forestry 66 619-21 (1968).

A twelve-point fire prevention program, followed by International Paper Company, is outlined. It emphasizes cooperation with state fire-prevention efforts, personnel participation, establishment of flexible communication lines (radios), a program of youth education, and a service of public information as to hazardous and fire-breeding conditions in local areas. The program, an apparent success, boasts less than one per cent of I-P lands in nine southern states burned per year between 1956 and 1965.

30. Reiter, F. W., "Solve Waste-Wood Disposal and Air Pollution Problems," Power 102, 114-5 (1958).

The solution was a unique combination of an incinerator and Dutch oven mounted alongside a pulverized burning boiler. A major problem in burning uniformly across the grate surface was studied. A spider like revolving head distributor was designed. Turning at about 90 r.p.m. it takes wood from the conveyor trough and feeds 6 round metal chutes leading to separate incinerator grate areas. The unit gives ideal combustion, maximum heat utilization, no smoke and no deposits in oven or boiler furnace. It requires practically no maintenance and saves more time than a carload of coal/week.

31. Shannon, L. J. and A. E. Vandergrift, "Particulate Pollution and Its Control," MRI Quarterly, 12-8 (1970-71).

A review of current particulate emissions and a forecast of future emissions indicates a need for wider use of the control devices already available.

32. Skvortsova, N. N. and S. N. Kimina, "Atmospheric Pollution with 3-4-Benzopyrene in the Vicinity of a Wood Products Chemical Plant," Gig. Sanit. 33 (2), 8-12 (1968).

Eventhough the system employed was presumably a closed one, there were appreciable amounts of 3-4-benzopyrene, resinous materials and phenol detected in the neighborhood. It is recommended that the sanitary protective region

around plants pyrolyzing wood be at least 100 m. in radius and that special care be taken to keep the process and products hermetically sealed.

33. Sterling, M., "Brush and Trunk Burning Plant in the City of Detroit," J. Air Poll. Control Assoc. 15, (12), 580-2 (1965).

Detroit City administration approved a \$250,000 expenditure for the design and installation of a unique 6 ton/hr. brush and trunk burning incinerator plant. Information is provided on the basic plant layout and design, wet fly ash collector configuration, operating and maintenance experience, and recommended changes for any future similar installations. Stack emission test data are also reported. Detroit City will no longer be required to burn brush and trunk waste in open fires.

34. Taylor, G. C., "Economic Issues in Controlling Agricultural Pollution," Amer. J. Agr. Econ. 51, 1182-8 (1969).

A detailed description of economic factors pertinent to meaningful solution of existing and future agricultural pollution problems is presented.

35. Tracy, R. H., Jr., "Changing the Fire Detection System," J. Forestry 66, 615-8 (1968).

After thorough evaluation and planning, the fire detection system of the Mount Hood National Forest was changed from ground detection to a system of air patrol supplemented by a few fixed ground stations. The steps involved in the evaluation and planning are described.

36. Wadleigh, C., "Wastes in Relation to Agriculture and Forestry," U.S.D.A. Misc. Pub. 1065, 112 pp. (1968).

Wastes resulting from agricultural and forestry operations are categorized and methods proposed for their disposal such that minimum pollution results are discussed.

37. Walker, W. R., "Legal Restraints on Agricultural Pollution," Agricultural Engineering 51, 636-7 (1970).

A discussion of legal implications of present and future agricultural processes that may contribute to pollution is presented.

38. Winkworth, R. C., "The Principles of Forest Fire Control--A Translation from the Military Principles of War," J. Forestry 67, 618-24 (1969).

A comparison of fighting fires to military type combat is made. Since fire control is a form of organized combat, military operations offer the most realistic and more highly developed precedents. The Principles of War, a recognized set of guidelines for military services, is the basis for a proposed set of Principles of Forest Fire Control. Selection and maintenance of the objective, appropriate readiness, continuous coverage by strategic disposition of forces, adaptability, mobility, coordination of effort, decisiveness, initiative, simplicity, and morale are the principles



discussed. It is emphasized that no one principle can stand alone; they are a set of interrelated principles that describe the requirements of sound forest fire strategy.

39. Wood "Waste" Utilization - Chemical and Mechanical Forest Products Research Guide in Fundamental and Applied Research, Second Edition, American Forest Products Industries, Washington, D. C., 71-4 (1945).

Past research by the Forest Products Laboratory, by University and other laboratories, by some of the forest, wood-working, and chemical industries, has supplied considerable knowledge on new methods of wood conversion and new products from wood and wood "waste". Research information on specific areas of interest is provided.

40. Zivnуска, J. A., "An Economic View of the Role of Fire in Watershed Management," J. Forestry 65, 596-600 (1968).

A critical comparison of economic factors to be considered when choosing between fire and mechanical methods of forestry management. Also discusses probabilistic estimates of escape of controlled fires beyond planned boundaries and the economic consequences.

#### B. Damage from Air Pollution

1. Anon., "Air Pollution: Plant Killer," Environ. Sci. and Tech. 4, 635-6 (1970).

A discussion of acute and chronic damage to plants from phytotoxic and secondary pollutants is presented. Specific effects are listed for SO<sub>2</sub>, F, O<sub>3</sub> and peroxyacynitrate.

2. Cobb, F. W., Jr., and Stasrk, A. B., "Decline and Mortality of Smog-Injured Ponderosa Pine," J. Forestry 68, 147-9 (1970).

Over a 3-year period 36 trees in a 150-tree plot in the San Bernardino Mountains of Southern California were killed by the western pine or the mountain pine beetle. Thirty-three of these exhibited advanced disease symptoms caused by photochemical air pollution. Of the 114 trees still living, 85 showed an increase in disease symptoms. The average disease rating in the 3-year period almost doubled. We have concluded that should air pollution continue unabated, ponderosa pine will be virtually eliminated from the forest stands in this area.

3. Hepting, G. H., "Damage to Forests from Air Pollution," J. of Forestry 10, 630-4 (1964).

Until a few years ago damage to forests from air pollution consisted mainly of localized but very severe cases of mortality and growth loss due to oxides of sulfur or to fluoride associated with ore reduction, with a minor contribution from other sources. In recent years oxidant damage, attributed largely to ozone in Los Angeles smog, is considered partly responsible for destroying ponderosa pine in the mountains east of that city. Oxidant has also been determined as the cause of a long-known needle blight

of eastern white pine now called emergence tipburn, and evidence is accumulating that the eastern white pine disease long known as chlorotic dwarf may be due to an abiotic air-borne agent. Mortality and growth loss of this species has also been occurring within a 20-mile radius of certain power plants consuming large quantities of soft coal. When potted ramets (vegetative reproductions) of selected sensitive white pine clones were exposed in an area embracing an industrial complex in east Tennessee, exposure for seven months resulted in uniformly severe damage. Ramets from resistant trees, similarly exposed, suffered no damage. Sensitive ramets kept out of the affected area remained healthy. New and important types of crop damage, including damage to trees, appears to be resulting from air pollution associated with our enormous urban development, with stack gases from new industrial processes, and with greatly increased emissions of stack gases from industrial plants using fossil fuels at rates far beyond consumption only 15 years ago.

4. Sinclair, W. A., "Polluted Air-Potent New Selective Force in Forests," J. Forestry 67, 305-9 (1969).

A review of some of the known acute and chronic effects of gaseous air pollutants on forest trees, with particular reference to ozone damage to pines, leads to perception of polluted air as a new selective force in temperate zone forests. This force is amplified by known interactions of air pollutants (as predisposing agents) with tree pests such as bark beetles, and by probable interactions with facultatively parasitic root and stem fungi, with insect defoliators, and with environmental factors such as drought. Heritable inter- and intraspecific variations in susceptibility to injury by polluted air and by specific pollutants are exploitable characteristics of trees, allowing selection of resistant trees and development of pollutant-sensitive trees as perennial bioindicators of air pollution. Experimental studies of the magnitude of air pollutant impacts on growth and reproduction of important tree species, of types of acute and chronic injury caused by various combinations of air pollutants, and of the impact of interactions of air pollutants with other agents are needed.

5. Wagner, R. V., "Survival of Coniferous Plantations Following Fires in Los Angeles County," J. Forestry 66, 622-5 (1968).

Coniferous plantations have been made throughout the San Gabriel Mountains of Los Angeles County, California, since the turn of the century, mostly by the Los Angeles County Department of Forester and Fire Warden. A majority of the plantations surviving the arid conditions of this area eventually have been destroyed by frequent brush fires, which would indicate a special need for protection. This study evaluated the effectiveness of several maintenance measures, and provides information for the future design and care of coniferous plantations.

### C. Photochemical Aspects

1. Altshuller, A. P. and J. Bufalini, "Photochemical Aspects of Air Pollution: A Review," Environ. Sci. & Tech. 5, 39-64 (1971).

The photochemical aspects of air pollution are reviewed through 1964. The topics covered include: nitric oxide oxidation and inorganic reactions, atomic oxygen and ozone reactions, singlet oxygen and its importance to air pollution, aldehyde and ketone photolysis, sulfur dioxide photolysis, synergistic effects, photooxidation of commercial solvents, product formation with emphasis on hydroperoxides, nitric acid and peroxybenzoyl nitrate, reactivity measurements including hydrocarbon consumption, nitric oxide oxidation, oxidant formation and eye irritation, aerosols, natural pollution, and actinometry. The effects of photochemical pollutants on plants are not covered. Suggestions for future research are also given.

2. Blacet, F. E., "Photochemistry in the Lower Atmosphere," Indus. and Eng. Chem. 44, 1339-42 (1952).

Some of the photochemical reactions which occur in air in the presence of sunlight are discussed. Ozone may be expected as a byproduct in the photolysis and oxidation of sulfur dioxide, nitrogen dioxide, aldehydes, and ketones. Hydrocarbons, in the presence of ozone and nitrogen dioxide in the air, may form organic lachrymators as their final oxidation products.

3. Darley, E. F., F. R. Burleson, E. H. Mateer, J. T. Middleton, and V. P. Osterli, "Contribution of Burning of Agricultural Wastes to Photochemical Air Pollution," J. Air Poll. Control Assoc. 11, (12), 685-90 (1966).

Agricultural wastes from orchards, grain fields and range lands are burned each year in California as the most practical means of ridding the land of these wastes. In order to determine the relative contribution of the burning of such material to photochemical air pollution, the effluent from 123 fires of known weights of range brush, both dry and green, barley and rice stubble, and prunings from various fruit and nut trees were monitored in a special tower which provided an open burning situation. Analyses were made for total hydrocarbon, expressed as C, by flame ionization detection, and for 24 individual hydrocarbons by gas chromatography, as well as for CO and CO<sub>2</sub> by infrared spectroscopy. A few analyses were made for oxides of N<sub>2</sub>. These data, coupled with temperature and airflow measurements allowed calculations to be made on pounds of effluent per ton of material burned and demonstrated that the emissions from agricultural burning are much less than from the automobile, a principle source of such emissions. (7 references).

4. Dutsch, H. V., "The Photochemistry of Stratospheric Ozone," Quart. J. Roy. Meteorol. Soc. 94, 483-97 (1968).

A short review of the photochemical theory in a 'dry' atmosphere is given. It is shown that the difference between theory and observations concerning the vertical gradient of N<sub>3</sub> (molecules of O<sub>3</sub>/cm<sup>3</sup>) in the upper stratosphere, where photochemical equilibrium may be assumed, can hardly be accounted for by observational uncertainties. It seems, however, not impossible to reconcile theory and observations by parametric adjustment. A semi-quantitative theory of O<sub>3</sub> in a 'wet' stratosphere is developed and the relative importance of different types of reactions is discussed. No reliable quantitative conclusion can be drawn at present due to large uncertainties in a number of parameters. In comparing vertical O<sub>3</sub> distribution



from this theory with observational data and considering the resulting change in relaxation times compared to the 'classical' theory, it is concluded that the influence of reactions of O and O<sub>3</sub> with active hydrogen compounds cannot be as strong as that derived from the use of Hunt's reaction rates. (Author's summary)

5. Faith, W. D., "The Photochemistry of Solvent Vapors," Air Eng. 10 (2), 16-7 (1968).

The photochemistry of solvent vapors is important as a contributing factor in the formation of smog. Reactive organics above some threshold value, well-mixed with oxides of nitrogen in a stagnant atmosphere under intense sunlight are the conditions necessary to produce photochemical smog. Since total reactive organics include the far more reactive hydrocarbons from automotive exhaust, the control of solvent vapor may be an expense that produces little public good.

6. Friedlander, S. K., and J. H. Seinfeld, "A Dynamic Model of Photochemical Smog," Environ. Sci. and Tech. 3, 1175 (1970).

A simplified kinetic scheme is proposed as a model for the photochemical smog reactions. Calculations based on the model lead to concentration dependences on time, similar in form to the experimental results for laboratory reaction chambers. To take into account the effect of atmospheric mixing processes on the chemical reactions, the Lagrangian similarity hypothesis for the diffusion of nonreactive components is extended to reacting species. This leads to a set of ordinary differential equations for the reactive species, of the type describing a chemical reactor of variable volume. As a preliminary example of the application of the model, a calculation is made for a single bimolecular reaction.

7. Glasson, W. A. and S. Tuesday, "Inhibition of Atmospheric Photooxidation of Hydrocarbons by Nitric Oxide," Environ. Sci. Tech. 4, 37-49 (1970).

The effects of nitric oxide concentration on the atmospheric photooxidation of propylene, ethylene, trans-2-butene, isobutene, and m-xylene have been investigated using long-path infrared spectrophotometry. Low concentrations of nitric oxide increased the photooxidation rate, while higher concentration inhibited the rate of hydrocarbon photooxidation measured either by hydrocarbon disappearance or product formation. The nitric oxide concentration necessary for the maximum photooxidation rate for a given hydrocarbon concentration decreased as the hydrocarbon concentration decreased, but, for the olefins studied, it was relatively independent of reactivity or structure. Decreased concentrations of hydrocarbon consistently decreased the rate of hydrocarbon disappearance and product formation at all nitric oxide concentrations investigated. The results of this investigation, together with atmospheric analyses, have established that nitric oxide inhibition is important in the photochemistry of polluted atmospheres.

8. Glasson, W. A. and S. Tuesday, "Hydrocarbon Reactivity and the Kinetics of the Atmospheric Photooxidation of Nitric Oxide," J.A.P.C.A. 20, 239-43, (1970).

The reactivity in the atmospheric photooxidation of nitric oxide has recently been determined for a large number of hydrocarbons. To aid in the application of these hydrocarbon reactivity measurements, the kinetics of the atmospheric photooxidation have been studied. The hydrocarbons investigated covered a wide range of reactivities and structures. The rate of nitric oxide photooxidation increases less than linearly with hydrocarbon concentration for all of the hydrocarbons studied. The degree of nonlinearity, however, varied with hydrocarbon structure and reactivity. The effect of the nitric oxide and the nitrogen dioxide concentrations on the rate of nitric oxide photooxidation also depended somewhat on hydrocarbon structure and reactivity. For all of the hydrocarbons studied, however, the nitric oxide photooxidation rate increased linearly with increased light intensity. The effect of complex hydrocarbon mixtures on the rate of nitric oxide photooxidation was investigated using three commercial gasolines. The nitric oxide photooxidation rates measures for these mixtures agreed within experimental error with calculated rates based on chromatographic analyses of the gasolines and the reactivity in nitric oxide photooxidation of the individual hydrocarbons in the gasolines.

9. Haagen-Smit, A. J., C. E. Bradley, and M. M. Fox, "Ozone Formation in Oxidation of Organic Substances," Indus. and Eng. Chem., 45, 2086-9 (1953).

A chemical characteristic of Los Angeles, Calif. smog is its oxidizing effect; oxidants, present in concentrations of 0.6 ppm, have been measured by various colorimetric methods. The oxidizing effect is attributed to a combined action of nitrogen oxides, peroxides, and ozone, counteracted by the reducing action of sulfur dioxide. Ozone and sulfur dioxide are present in concentrations of 0.3 and 0.1-0.2 ppm, respectively. Data for the formation of ozone as determined by rubber cracking are tabulated. The simultaneous presence of hydrocarbons and nitrogen oxides accounts for the high ozone content.

10. Hanst, P. L., E. R. Stephens, and W. E. Scott, "Reactions Involving Ozone, Nitrogen Dioxide, and Organic Compounds at Low Concentrations in Air," Jour. Air Poll. Control Assoc., v. 5, 2190225, 244, (1956).

Ozone is probably the oxidizing agent in smog. Experiments were performed by the Franklin Inst., Philadelphia, Pa., which describe how ozone is formed, and what part ozone plays in producing the objectionable features of smog. The following reactions are described: 1. ozone-olefin; 2. nitrogen dioxide-olefin; 3. ozone-saturated hydrocarbons; 4. nitrogen dioxide-saturated hydrocarbons; 5. ozone-aldehyde; 6. nitrogen dioxide-aldehyde; 7. peroxy acid-nitrogen dioxide; and 8. biacetyl-aldehyde-air. A summary is given, and conclusions are drawn.

11. Katz, M., "Photochemical Reactions of Atmospheric Pollutants," Can. J. Chem. Eng. 48, 3-11, (1970).

The photochemical reactions that may occur in polluted urban atmospheres represent a highly complex system. Significant absorbers of solar energy in the wavelengths above 3000 Å that penetrate into the lower atmosphere include nitrogen dioxide, nitrous and nitric acid, sulfur dioxide, hydrocarbons,

many other organic compounds and aerosols that are present as pollutants. In this photochemical process, organic and other free radicals are formed by primary and secondary photodissociation reactions. These free radicals may undergo reactions leading to the formation of short or long chains containing a number of sequence steps until the chain is terminated by some chain-breaking mechanism. Since the pollutants and their atmospheric environment represent a highly variable system in composition, concentration, humidity, temperature, intensity, and angle of incidence of sunlight, it is difficult to relate the results of controlled laboratory experiments directly to field conditions. Nevertheless, the efforts of various research workers have contributed a considerable amount of knowledge as to kinetics, mechanisms and nature of reaction products involved in these overall photochemical processes. The mechanisms postulated by research groups in the field are discussed in detail. The present status of research in this field emphasizes the complexity of photochemical reactions of atmospheric pollutants. In spite of the many difficulties, this subject represents a fruitful and challenging subject for investigation. Sulfur dioxide, oxides of nitrogen, hydrocarbons, other reactive organic substances and particulates are always present in urban atmospheres. During temperature inversions and periods of stagnant air, these atmospheric pollutants may accumulate to relatively high concentration levels and be subjected to prolonged solar irradiation with the production of reaction products that could be photo-toxic, detrimental to health or reduce visibility. (Author's summary, modified)

12. Levi, C. R., "Atmospheric Ozone: An Analytical Model for Photochemistry in the Presence of Water Vapor," J. Geophys. Res. 74 (2), 417-26 (1969).

An approximate analytic model of  $O_3$  photochemistry including reaction with hydrogen compounds is developed for the atmospheric region between 15 and 60 km. The reaction scheme is a simplified version of that used by B. G. Hunt. The model is used to study time-dependent processes, the sensitivity of the equilibrium-concentration values to uncertainties in reaction rates, and the variations in the equilibrium ozone concentration with latitude and season. There are five main results. 1.  $O_3$  loss in the model depends on the ratio of the rate of production of  $O(^1D)$  and the rate of dissociation of  $H_2O$  by  $O(^1D)$ , but the loss rate and equilibrium  $O_3$  concentration are not very sensitive to this ratio. 2. Below 40 km the relevant reaction rates are comparatively certain and the  $O_3$  concentration is very likely to be controlled by reactions of atomic oxygen with OH and  $HO_2$ . 4. As a consequence of (3), the  $O_3$  concentration near the stratopause is probably not sensitive to temperature, and the dynamical damping sometimes attributed to this temperature sensitivity is likely to be unimportant. 5. If the model is correct, the photochemical time scale for  $O_3$  is much less than it would be if only  $O_2$  reactions control  $O_3$ ; consequently, in low latitudes,  $O_3$  may be subject to photochemical influence down to as low as 15 km. (Abstract)

13. Raff, R. A. and C. M. Meaburn, "Photochemical Reaction Mechanisms for Production of Organic Compounds in a Primitive Earth Atmosphere," Nature 221, 459-60 (1969).

Thermodynamic considerations dictate the existence of a reducing atmosphere on the earth during the synthesis of prebiological organic compounds.



Some of the reactions by which a primitive atmosphere might have given rise to reduced compounds of C and N are explored.

14. Rasmussen, R. A., "Isoprene: Identified as a Forest-Type Emission to the Atmosphere," Environ. Sci. and Tech. 4 (8), 667 (1970).

The hemiterpene isoprene (2-methyl-1, 3-butadiene) until recently has not been considered to be present in natural plant products. Direct gas chromatographic, infrared, and mass spectrometric analyses of the air in contact with the plant foliage for five common tree species confirm previous observations (Rasmussen, 1964) of the existence of isoprene as a plant product. Preliminary data from surveying the dominant forest tree species of North America indicate that the frequency of occurrence of isoprene is similar to that of alpha-pinene although species differ. Isoprene has been resolved directly from the out-of-doors air over mango foliages in Panama at concentrations of 0.5 to 24 p.p.b. in 5 ml. of air. The biological and air chemistry fates of isoprene are discussed.

15. Stephens, E. R., and others, "Recent Developments in the Study of the Organic Chemistry of the Atmosphere," J. Air Poll. Control Assoc. 6 159-65 (1956).

The experiments show that ozone detected during a Los Angeles, Calif. smog attack can be accounted for by photochemical reaction of nitrogen dioxide with organic compounds. It has been suggested that the situation might be alleviated by reducing the amount of nitrogen oxides released into the atmosphere. It would be of interest to know whether ozone is produced directly from the nitrogen dioxide by the oxygen-atom mechanism outlined or whether it is a byproduct of oxidation reactions such as the diacetyl-photolysis experiment described. The sum of evidence appears to favor the former mechanism. The amount of diacetyl necessary to produce a significant ozone concentration is considerably greater than the concentration of atmospheric contaminants. Furthermore, diacetyl is apparently in a class by itself in regard to ozone formation through photolysis if systems containing combined nitrogen are excluded. Even on the basis of the mechanism involving the formation and photolysis of compound X, it would be hasty to conclude reduction in the amount of nitrogen oxides emitted into the atmosphere would proportionately reduce either the ozone concentration or smog severity (these 2 quantities are not necessarily directly proportional). The combined nitrogen may pass through this cycle many times, and may produce an ozone concentration not directly proportional to the initial nitrogen-dioxide concentration. The experiments with the 2 types of gasoline illustrate this point. (Authors' abstract).

16. Stephens, E. R. and M. A. Price, "Atmospheric Photochemical Reactions in a Tube Flow Reaction," Atmos. Environ. 3, 513-82 (1969).

The complexities of atmospheric chemistry lead to the expectation that changes in the nature and not just in the amount of photochemical smog will result from the current program for controlling hydrocarbon emissions. When the amount of reactive hydrocarbon is no longer sufficient to convert all the nitric oxide to products, marked decreases in most smog symptoms should be observed but there may also be an appreciable increase in nitrogen

dioxide exposure. These changes were studied in a transparent flow reactor using artificial ultraviolet irradiation. The output of ozone and peroxyacetyl nitrate decreased sharply when the amount of hydrocarbon used was not sufficient to convert all the input nitric oxide to nitrogen dioxide. The nitrogen compounds detected in the output (nitric oxide, nitrogen dioxide, peroxyacetyl nitrate and trace amounts of alkyl nitrate) fell short of accounting for all the nitric oxide in the input. Each molecule of propylene or cis-2-butene consumed caused, at maximum, about two molecules of nitric oxide to be converted to nitrogen dioxide. (Author's abstract)

17. Thomas, M. D., "Photochemical Smog," Air Quality Monograph 69-6, New York, American Petroleum Institute, (1969).

Two principal types of urban air pollution are currently recognized: 1. the chemically reducing type in which sulfur dioxide is an important constituent of the mixture derived largely from the combustion of sulfur bearing ores, coals, and oils together with soot, fly ash, smoke, and partially oxidized organic compounds; and 2. the chemically oxidizing type--the so-called photochemical smog--that is practically free of sulfur dioxide but contains substantial amounts of nitrogen oxides, ozone, ozonated olefins and organic peroxide compounds, together with many other compounds from the partially burned fuel, in addition to aerosols formed by the polymerization of the organic reaction products which, along with sulfuric acid aerosols, reduce visibility in the atmosphere. This paper discusses the constituents and reactions of photochemical smog which have been studied intensively in the Los Angeles area and elsewhere.

18. Tuesday, C. S., and Glasson, W. A., "Hydrocarbon Reactivity and the Kinetics of the Atmospheric Photooxidation of Nitric Oxide," J. Air Poll. Control Assoc. 20 (4), 239-43 (1970).

The reactivity in the atmospheric photooxidation of NO has recently been detected for a large number of hydrocarbons. To aid in the application of these hydrocarbon reactivity measurements, the kinetics of the atmospheric photooxidation was studied. The hydrocarbons investigated covered a wide range of reactivities and structures. The rate of NO photooxidation increases less than linearly with hydrocarbon concentration for all of the hydrocarbons studied. The degree of nonlinearity, however, varied with hydrocarbon structure and reactivity. The effect of the NO and the NO<sub>2</sub> concentrations on the rate of NO photooxidation also depended somewhat on hydrocarbon structure and reactivity. For all of the hydrocarbons studied, however, the NO photooxidation rate increased linearly with increased light intensity. The effect of complex hydrocarbon mixtures on the rate of NO photooxidation was investigated by using 3 common gasolines. The NO photooxidation rates measured for these mixtures agreed within experimental error with calculated rates based on chromatographic analyses of the gasolines and the reaction in NO photooxidation of the individual hydrocarbons in the gasolines.

19. Tuesday, C. S., and Glasson, W. A., "Inhibition of Atmospheric Photooxidation of Hydrocarbons by Nitric Oxide," J. Air Poll. Control Assoc. 20, 239-43 (1970).



The effects of NO concentration on the atmospheric photooxidation of propylene, ethylene, trans-2-butene, isobutene, and m-xylene were investigated using low path ir spectrophotometry. Low concentrations of NO increased the photooxidation rate, while higher concentrations inhibited the rate of hydrocarbon photooxidation, measured either by hydrocarbon disappearance or product formation. The NO concentration necessary for the maximum photooxidation rate for a given hydrocarbon concentration decreased as the hydrocarbon concentration decreased, but, for the olefins studied, it was relatively independent of reactivity or structure. Decreased concentrations of hydrocarbon consistently decreased the rate of hydrocarbon disappearance and product formation at all NO concentrations investigated. The results of this investigation, together with atmospheric analyses, have established that NO inhibition is important in the photochemistry of polluted atmosphere.

#### D. Analytical Techniques

1. Altshuller, A. P., "Determination of Formaldehyde in Gas Mixtures by the Chromotropic Acid Method," Anal. Chem. **33**, 621 (1961).

The method developed by West and Sen has been applied to the detection of HCHO in gaseous chromotropic acid in concentrated  $H_2SO_4$  is more efficient than the one charged with 1%  $NaHSO_3$  or  $H_2O$ .  $NaHSO_3$  is a very efficient collector if used with a gritted glass bubbler. Collection of the sample directly in concentrated  $H_2SO_4$  results in a 10-fold increase in sensitivity over  $NaHSO_3$ .  $NO_2$ , aldehydes, ketones, and phenols do not interfere in concentrations normally present in combustion products. Higher alcohols and phenols will result in a negative interference if present in concentrations higher than that of HCHO. Olefin interferences can be reduced by a rapid flow rate of 1l./min. through the impinger. Interference from aromatic hydrocarbons can be avoided if HCHO is collected in  $NaHSO_3$ .

2. Bellar, T. A., and J. E. Sigsby, Jr., "Direct Gas Chromatographic Analysis of Low Molecular Weight-Substituted Organic Compounds in Emissions," Environ. Sci. and Tech. **4**, 150-6 (1970).

This paper describes an automated, gas chromatographic method for direct analysis of  $C_{2-4}$  aldehydes,  $C_{3-4}$  ketones, and various other O-, N-, and halogen-containing organic compounds present in combustion effluents. Retention times are given for a great variety of compounds this system is capable of analyzing. Examples of chromatograms from analysis of samples of auto exhaust, trench incineration effluents, and ambient air are included. The limit of detection for the system is 0.05 ppm of AcH.

3. Bethea, R. M., and M. C. Meader, "Gas Chromatographic Analysis of Reactive Gases in Air," J. Chromatogr. Sci. **7**, 655-7 (1969).

The ability of various columns for the qualitative separations of mixtures of reactive ( $NO$ ,  $NO_2$ ,  $SO_2$ ,  $HCl$ ,  $H_2S$ ,  $Cl_2$ ,  $NH_3$ ) and other gases ( $CO_2$ ,  $N_2O$ ) in air was evaluated. No single column was found which was

effective for the separation of these compounds. A two section column of Porapak Q and Porapak R provided adequate separation of NO and air. The  $\text{N}_2\text{O}-\text{CO}_2$  separation was best on a QF-1 Fluoro column.  $\text{Cl}_2$  and  $\text{SO}_2$  can be analyzed on either of two columns: silicone oil SF-96 or triacetin. These columns were also effective in making the air- $\text{CO}_2$ - $\text{NH}_3$  separation. Symmetric, reproducible sharp peaks were obtained for  $\text{NO}_2$  on Kel-F 90 and Fluorolube HG 1200 columns. Both of these columns while providing a somewhat inferior peak shape, completely separated  $\text{NO}_2$  from all other compounds tested.

4. Commins, B. T. and A. J. Lindsey, "The Determination of Phenols by Chromatography and Spect photometry of Their Methyl Ethers. Part III. The Determination of Phenols in Wood Smoke," Anal. Chim. Acta. (Amsterdam) **15**, 554-6 (1969).

The method previously developed for the determination of phenols by chromatography and spectrophotometry of their methyl ethers has been applied to their determinations in wood smoke. (10 references).

5. Innes, W. B., and A. J. Andreatch, "Hydrocarbon and Carbon Monoxide Analysis by the Selective Combustion Method," Environ. Sci. and Tech. **4**, 143-9 (1970).

An instrument involving heat effects in catalytic beds was developed and applied to measurement of CO and hydrocarbons in an air stream. The temperature rise from slug sample injection into an air stream with constant flow rate was found to give a linear and selective measure of total hydrocarbons injected with a vanadia catalyst and of total CO with a hopcalite catalyst at the levels normally encountered in exhaust gases. The response to hydrocarbons in vehicle exhaust gas which is substantially additive can be tailored to correspond reasonably well with either photochemical reactivity or nondispersive hexane-sensitized ir, although response for olefins and aromatics relative to paraffins is higher than for the ir method. Response and recovery times allow rapid measurement and depend primarily on catalyst bed diameter. Although the major use of the instrument appears to be for vehicle exhaust analysis, suitable modification would make it useful for air monitoring and chromatographic detection.

6. Kaiser, E. R., "Chemical Analyses of Refuse Components," Proceedings of 1966 National Incinerator Conference, New York, N.Y., 84-7 (1966).

The proximate and ultimate analyses of 20 constituents of municipal and commercial refuse are presented, together with the calorific values. The analyses are useful to incinerator engineers as they provide a basis for calculating air requirements, flue gas volumes, and heat and material balances.

7. Lustre, A. O., and P. Issenberg, "Volatile Components of Hardwood Sawdust Smoke: Components of Phenolic Fraction," J. Agr. Food Chem. **17**, 1387 (1969).

Thirty-one compounds in the phenolic fraction of mixed hardwood smoke were separated by gas chromatography on a variety of columns. They were identified by comparison of their retention times and their mass and infrared spectra with known authentic compounds except that in cases where reference materials were not available, degradative and synthetic reactions to known standard compounds were employed. The presence of compounds previously reported was confirmed, and compounds were identified that have not been previously reported. Condensates prepared from mixed hardwood sawdust and from hickory sawdust smoke were compared and found to contain the same compounds.

8. Lyardo, R. E. and B. I. Vasilev, "Chromatographic Method of Completely Automatic Analysis of Flue Gases," Thermal Engr. 9, 70-3 (1969).

A chromatographic system for determination of combustible and incombustible components of combustion products on two chromatographs is discussed. Parallel columns with molecular made possible a time of analysis of approximately 4.5 minutes.

9. Rhee, K. S., and Bratzler, L. H., "Polycyclic Hydrocarbon Composition of Wood Smoke," J. Ford. Sci. 33, 626-32 (1968).

Eleven polycyclic hydrocarbons derived from predominantly hard maple sawdust smoke have been separated and identified. The hydrocarbons were isolated and separated stepwise by a combination of liquid-liquid extraction, chromatography on silicic acid, thin-layer chromatography with acetylated cellulose powder and chromatography on aluminum oxide. They were characterized by ultraviolet and fluorescence studies on the fractions thus obtained from the aluminum oxide column. The polycyclic hydrocarbons found in the hardwood sawdust smoke include naphthalene, acenaphthene, fluorene, phenanthrene, anthracene, pyrene, fluoranthene, 1,2-benzanthracene, chrysene, 3,4-benzopyrene and 1,2-benzopyrene. Analysis of whole wood smoke and the vapor phase obtained by an electrostatic air filter showed only quantitative differences.

10. Wasserman, A. E., "Organoleptic Evaluation of Three Phenols Present in Wood Smoke," J. Food Sci. 31, 1005, (1966).

Guaiacol, 4-methyl guaiacol and 2,6-di-methoxyphenol, components of wood smoke condensates, were evaluated organoleptically. Mean panel thresholds of the taste and odor in water and the odor in mineral oil were determined for each compound. The majority of the panel characterized the compounds as being smoky in odor and taste, although phenolic characteristics were also present. The relative effectiveness of each compound in the over-all flavor picture was shown by the ratio (concn. in smoke/threshold concn.) Guaiacol had the largest index, whereas 2,6-dimethoxyphenol, which was present in smoke condensate in greatest concentration, had a considerably low value. (Bibliography included).

## V. CONCLUSIONS AND RECOMMENDATIONS

An analysis of research performed to date indicates that the impact of the products of wood combustion on the national air pollution level is very small. It has been estimated that the annual contribution of hydrocarbons from wood burning operations is less than the daily yield from combustion of fossil fuels.

Although chemical compounds have been identified from wood burning that could contribute to photochemical smog formation, there is no laboratory evidence to confirm this possibility. The most obvious air pollution objection is the nuisance associated with the large particulate burden that results from open burning of woody fuels and the impaired visibility that results. Thus, the major objection, at this time, to air pollutants from wood burning is the impairment of the environment in the immediate and near vicinity of such burning operations.

There is a general paucity of hard data regarding woody combustion pollution, and research is needed to supply quantitative data. The degree and extent of pollution that results from combustion of woody fuels indigenous to the Southeast is almost completely unresearched. Consequently the following major research objectives are recommended:

1. Identify the products of combustion of woody fuels native to the Southeast.
2. Determine the concentrations of gases and particulate matter from controlled and field burns of Southern woody fuels.
3. Forests are sources of natural pollutants (those not necessarily associated with burning), e.g., alpha-pinene is found in substantial amounts in the vicinity of pine forests and could contribute to photochemical smog even in the absence of any combustion processes. Isoprene has